CONSTRUCTION MATERIALS

DOI 10.15826/rjcst.2017.1.009 УДК 666.9

Lipunov I. N.[1], *Pervova I. G.*[2], *Nikiforov A. F.*[3]

[1–3] Ural State Forestry Engineering University
Yekaterinburg, Russia

E-mail: [1]*biosphera@usfeu.ru*

MAGNESIUM CEMENTS DERIVED FROM TECHNOGENIC RAW MATERIALS

Abstract. The paper presents a comprehensive study of sludge forming in carnallite chlorinators while magnesium manufacturing, VSMPO-AVISMA Corporation, Russia. The sludge contains two principal products MgO and MgCl2 used in magnesium-based cements manufacture. Chemical and phase compositions of the sludge, mass ratio of magnesium components presented in the sludge, reaction capacity of MgO extracted from the sludge, MgO binding properties, the sludge properties, its radiation safety, and sanitary and epidemiological safety have been thoroughly studied. It has been concluded that it was made the conclusion about the possibility of recovering and recycling the sludge to magnesium cementing powder.

The kinetics and thermodynamics of the hydration of magnesium oxide in the sludge were studied. The study has proved high chemical reactivity of magnesium oxide and its ability to form a magnesium mixture followed by the forming the crystallohydrate structures which are characteristic for the magnesium mixture, made of caustic magnesite gaged by magnesium chloride solution. The optimal parameters for the process of forming the magnesium mixture have been established.

Keywords: technogenic raw materials, regeneration, magnesium cements.

Липунов И. Н.[1], *Первова И. Г.*[2], *Никифоров А. Ф.*[3]

[1–3] Уральский государственный лесотехнический университет,
Екатеринбург, Россия

E-mail: [1]*biosphera@usfeu.ru*

МАГНЕЗИАЛЬНЫЕ ЦЕМЕНТЫ, ПОЛУЧЕННЫЕ ИЗ ТЕХНОГЕННОГО СЫРЬЯ

Аннотация. Проведено комплексное исследование шламов карналлитовых хлораторов магниевого производства ОАО «Корпорация ВСМПО-АВИСМА», содержащих в своем составе два основных магнезиальных компонента MgO и MgCl2, участвующих в формировании магнезиальных цементов. На основании изучения химического, фазового состава шлама, массового соотношения в шламе магнезиальных компонентов, реакционной способности MgO, выделенного из шлама, вяжущих свойств MgO и самого шлама, его радиационной и санитарно-эпидемиологической безопасности сделан обоснованный вывод о практической возможности регенерации и последующей утилизации шлама в порошок магнезиальный вяжущий. Результаты изучения кинетики и термодинамики процессов гидратации оксида магния в шламе подтвердили его высокую химическую активность и способность к образованию магнезиального теста с последующим формированием кристаллогидратных структур, характерных для магнезиального теста, полученного при затворении вяжущего каустического магнезита раствором хлорида магния. Установлены оптимальные параметры процесса образования магнезиального теста в системе шлам — вода.

Ключевые слова: техногенное сырье, регенерация, магнезиальное вяжущее.

Introduction

Inorganic cementing materials featured by magnesium-type hardening are widely used in construction, thermal and sound insulation materials, magnesium flooring, products for corrosion protection of underground communications, and strip foundations. Raw materials to produce magnesium cements are natural minerals magnesium carbonate, dolomite, and brucite. However, the shortage of natural raw materials and the high cost of magnesium salts added to mix caustic magnesites restrict their using in construction industry.

These have resulted to developing alternative raw materials to produce magnesium-type hardening cements. Magnesium-containing technogenic raw materials provide sustainable solutions through the recycling of waste so they extend raw materials range to produce advanced magnesium cements [1–3].

Magnesium metal manufacturing wastes so-called the carnallite chlorinator sludge containing two principal products MgO and $MgCl_2$ to produce magnesium-based cements are the most promising.

The aim of the research was to conduct a number of comprehensive investigations to determine chemical, phase, and radionuclide compositions of the sludge forming during magnesium metal manufacturing, VSMPO-AVISMA Corporation, Russia; the hydration kinetics of MgO containing in the sludge, binding properties of both MgO and the sludge, and to develop technology for recovering and recycling the sludge to magnesium cementing powder.

Research methods

Preliminary preparation (regeneration) of the sludge for the investigation was carried out mechanically by crushing, grinding to the dispersed phase between 200 and 100 microns and fractionating. A laboratory unit for fractionation consists of a jaw crusher and ball mill equipped with a cyclone for dust collection. Screen size gradation was used to fractionate the powder. The sludge prepared for the investigation was stored in hermetic containers to avoid the hydration of MgO containing in the sludge.

Quantitative determination of the chemical composition of the sludge were investigated by chemical and x-ray diffraction analyses. Chlorides of alkali metals were determined by flame spectrophotometry [4]; magnesium-containing compounds were done by complexometric titration [5]. X-ray diffraction analysis [6] was also used to reveal the phase state of individual compounds containing in the sludge. X-ray patterns of the studied sludge samples were shot on auto-diffractometer STADI- (STOE, Germany), copper Kα radiation, an interval of angles 2θ from 5° to 80°, step of 0.02°. "Base powder standards JCPDS-ICDD PDF2" (ICDD, USA, Release 2003) was used for compound identification.

Reactivity of magnesium oxide extracted from the sludge, was determined by the degree of its hydration at temperatures of 40, 60, and 80 °C in systems $MgO–H_2O$ and $MgO–MgCl_2–H_2O$. Magnesium oxide was extracted from the sludge by hydroleaching the soluble salts ($MgCl_2$, KCl, NaCl); the formed heterogeneous system was separated by filtration, the resulting residue after filtration was washed by water, then by acetone, made it air-dried and kept in hermetic containers. According to X-ray diffraction analysis the MgO content in the residue was 97%. The hydration of magnesium oxide was investigated by thermogravimetric analysis [7]. Derivatograms of hydrated magnesium oxide samples were being filmed with derivatograph Q-1500D. The investigated samples were being heated in air medium in crucibles to a temperature of 700 °C at rate of 10 deg·min$^{-1.}$ The sample mass was 1000 mg, the sensitivity of DTA–250, both TGP and TG — 500 μV. The product compositions after the hydration were established by x-ray diffraction analysis and infrared spectroscopy [8].

The experimental values of the degree of magnesium oxide hydration were calculated according to derivatograms. To do this, the established ratio of the mass loss in the samples were related to stoichiometric amounts of products after thermal decomposition of crystallohydrate structures $Mg(OH)_2$ and $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$. The rate of the magnesium oxide hydration in the investigated systems was calculated according to the results of kinetic studies on the equations of Kolmogorov–Erofeev and Sakovich [9].

The role of magnesium oxide in the formation of crystallohydrate structures was experimentally revealed according to x-ray diffraction analysis. Normal density magnesium mixture, start and final moments of its setting, formed when mixing MgO with $MgCl_2$ solution, and the sludge — with water, were determined in accordance with GOST 310.3–76 using Vika tool [10]. Binding properties of MgO and sludge were estimated by the compressive strength values of the laboratory samples of magnesium stone, shaped in the form of cylinders, diameter and height 20mm and seasoned for 3, 7, and 28 days for strength developing. The samples were subjected to destruction under dynamic load test on a hydraulic press 2 НГ–10 with evenly increasing speed of 1 mm/s [11].

Toxicological tests of the sludge were carried out in the Center of State Sanitary and Epidemiological Supervision in Sverdlovsk region. The natural radioactivity of the sludge were determined by the method of γ — spectrometry [12] using a spectrometer СЭГ-1 П.

Results

Methods of chemical analysis identified the s ubstance composition of the sludge, which is composed of 98.4 % of chlorides of Na, K, Mg, and oxide of Mg. Impurity compounds containing in the sludge are oxides of Si, Fe, Al, and chlorides of Ca and Ba, the number of which is $4{,}0 \cdot 10^{-1}$, $2{,}7 \cdot 10^{-1}$, $9{,}0 \cdot 10^{-2}$, $2{,}0 \cdot 10^{-3}$ $4.3 \cdot 10^{-4}$ % respectively.

When studying several sets of sludge samples taken at the site for dehydration of carnallite melting in VSMPO-AVISMA Corporation, Russia, it was revealed that the vertical cut of the sludge ingot is a "layer cake" and each layer is differently coloured: white (upper layer), grey (middle layer) and yellow (bottom layer). The differently coloured sludge samples were analysed to detect quantitative content of the main chemical compounds and their phases by chemical and X-ray diffraction analyses (Table 1).

The white sludge samples are characterized by high content of the lighter and water-soluble chemical compounds $MgCl_2$, KCl and NaCl, which when cooling the sludge melting, "are getting salted out" to the upper part of the ingot. MgO is almost absent in the upper part.

The grey sludge samples are presented by magnesium components (MgO, $MgCl_2$), their contents are 35,0 и 27,3 % respectively according to chemical analysis.

In the yellow sludge samples MgO is predominant by weight; with higher density in comparison to other chemical compounds, MgO "precipitates" from the melting to the bottom part of the sludge ingot.

composition, especially magnesium components, throughout its volume.

Because of high sensitivity of the magnesium binding materials technology to MgO activity, as well as the lack of understanding the mechanism of underlying processes of magnesium cement formation, especially when using technogenic materials, we have investigated the reactivity of MgO extracted from the regenerated sludge.

Table 1

Mass fraction (%) of main chemical compounds in the differently coloured sludge samples and in the averaged sample

Sludge color	Chemical analysis				X-ray diffraction analysis			
	MgO	$MgCl_2$	NaCl	KCl	MgO	$KCl{\cdot}MgCl_2{\cdot}6H_2O$	$KCl{\cdot}MgCl_2$	NaCl
White	0,7	47,4	2,7	18,1	*	8,0	80,5	5,9
Grey	35,0	27,3	1,7	10,0	31,4	51,5	*	3,8
Yellow	56,6	18,1	1,1	6,3	72,6	46,2	*	1,3
Averaged	42,3	27,9	2,0	16,6	63,3	34,6	*	2,2

* the compound is not presented in the studied sludge sample

According to X-ray diffraction analysis the chemical composition of white coloured sludge samples is characterized by the presence of three separate phases: the separate phase NaCl (d = 0,282 and 0,199 nm), the phase of anhydrous carnallite $KCl{\cdot}MgCl_2$ (0,285; 0,248; 0,246 and 0,175 nm), and the phase of hexaquacarnallite $KCl{\cdot}MgCl_2{\cdot}6H_2O$ (d = 0,333; 0,298; 0,239; 0,234 nm). The chemical composition of the grey and yellow coloured sludge samples are also characterized by the presence of three separate phases: the phase of hexaquacarnallite $KCl{\cdot}MgCl_2{\cdot}6H_2O$, the phase NaCl, and the phase MgO (d = 0,211; 0,149; 0,122 nm).

The uneven distribution of chemical compounds along height and across volume of the sludge ingot forming in a mold is explained by sedimentation and stratification of the chemical components of the sludge in mixers and molds during cooling and crystallisation of the sludge melting.

The averaged (recovered) sludge sample was obtained by mixing representative differently coloured sludge samples in equal mass ratio, further crushing, grinding and thorough mixing towards grey powder with definite particle sizes. According to x-ray diffraction analysis the chemical components in the averaged sample are presented the same phases as in the grey and yellow coloured sludge samples, however they are evenly spread throughout the sample. The mass ratio MgO: $MgCl_2$ for the recovered sludge is 1: 0,66 which is close to the optimal ratio of these components while forming magnesium cement from caustic magnesite and magnesium chloride solution (1: 0,62÷0,65).

Thus, the results of these studies showed the necessity of regeneration of the original sludge to achieve homogeneity and constancy of the chemical

The background for such research was the developing knowledge of the kinetics of the MgO hydration in the system $MgO–H_2O$ and $MgO–MgCl_2–H_2O$ at different temperatures.

The MgO hydration in the investigated systems is described by the following equations:

$$MgO + H_2O = Mg(OH)_2,$$

$$3MgO + MgCl_2 + 11H_2O = 3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O.$$

The values of the MgO hydration degree were evaluated in accordance with the endothermic effects in the derivatograms of hydrated samples. It was found the values gets higher with temperature rising and are significantly higher for the system $MgO–MgCl_2–H_2O$ (Table 2). The fact indicates that technogenic MgO has higher chemical activity when it interacts with $MgCl_2$ solution, which is in good agreement with the scientific report data concerning the reactivity of caustic magnesia binder [13].

Table 2

Values of the MgO hydration degree in the investigated systems at different temperatures and exposure time 6 h

System	Hydration degree (α, %)		
	Temperature, °C		
	40	60	80
$MgO–H_2O$	4,1	17,2	34,4
$MgO–MgCl_2–H_2O$	22,5	61,8	75,3

The values of the hydration rate constants calculated by mathematical treatment of kinetic curves of MgO hydration degree in the investigated systems [9] are given in Table 3.

The values of the hydration rate constants gets higher with temperature rising; the values for the system

$MgO–MgCl_2–H_2O$ appeared to be higher by 1000, 10, and 1,5 times at temperatures 40, 60, and 80 °C respectively.

Table 3

Values of the MgO hydration rate constants in systems $MgO–H_2O$ and $MgO–MgCl_2–H_2O$

System	Hydration rate constants		
	Process temperature, °C		
	40	60	80
$MgO–H_2O$	$3{,}077\cdot10^{-5}$	$5{,}026\cdot10^{-2}$	$1{,}871\cdot10^{-1}$
$MgO–MgCl_2–H_2O$	$2{,}513\cdot10^{-2}$	$1{,}827\cdot10^{-1}$	$2{,}964\cdot10^{-1}$

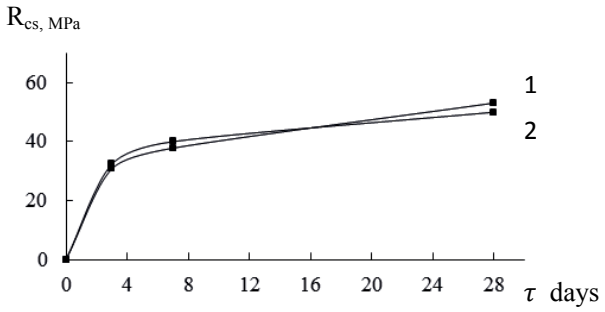

Fig. 1. Relation between ultimate compressive strength and hardening time for the laboratory samples formed from the mixture of MgO and $MgCl_2$ solution at S: L = 1,96 (1) and sludge with water at S: L = 0,43 (2)

mixture formation with following its hardening and the crystallohydrate structures forming: the mass ratio MgO and aqueous solution $MgCl_2$ with density 1.2 g/cm^3 (1,96), temperature (80 °C) and time of pre-heating the reaction mixture (30 min), under these parameters the start and final setting time (20 and 60 min respectively) correspond to the normative figures for cementitious caustic magnesite.

Laboratory samples formed from the magnesium mixture and seasoned for strengthening for 3, 7, and 28 days have a maximum compressive strength of 18.7; 31.2 and 53.1 MPa respectively.

Kinetic studies of the set of laboratory sample strength showed that the process of forming crystallohydrate structures has intensively run during the first 7 days and by the finish of the period the magnesium cement is getting 60 % of the grade strength (Fig. 1). After 28 days forming crystallohydrate structures of magnesium cement is almost completed and it has the maximum value of the compressive strength.

Forming crystallohydrate structures in the samples aged of 28 days of hardening time was confirmed by the presence in the X-ray diffraction lines d = 0.478, 0.237, 0.180, 0.157, and 0.148 nm, corresponding to the hydrated form of the composition $Mg(OH)_2$ and d = 0.240, 0.226, and 0.198 nm corresponding to the crystallohydrate composition $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (Fig. 2).

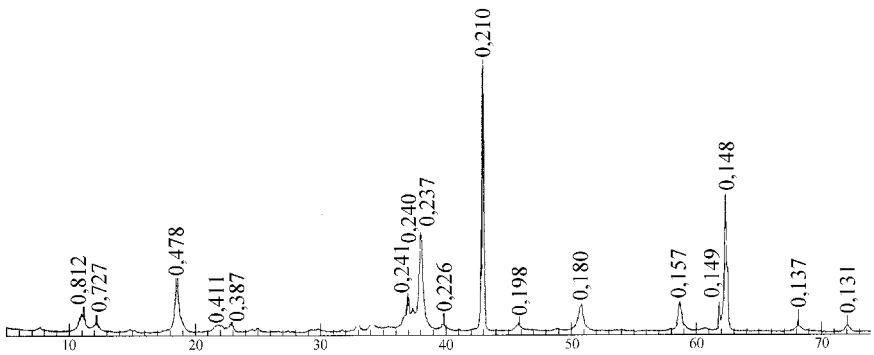

Fig. 2. X-ray pattern of the sample, formed from MgO, gaged with $MgCl_2$ solution (ρ = 1.20 g·cm^3) and aged 28 days

Study of hydration process kinetic showed that magnesium oxide containing in the sludge has high chemical reactivity and, being mixed with $MgCl_2$ solution, forms magnesium mixture with following forming crystallohydrate structures, which are the basis for magnesium cement.

MgO involvement into the processes of forming crystallohydrate structures of magnesium cement was experimentally established. Sample weights of magnesium oxide for making magnesium mixture gaged by $MgCl_2$ solution with different mass solid: liquid ratio (S: L). Optimal parameters for processes of magnesium

Presence of hydrate formed in the magnesium stone is also evidenced by the intensive absorption band appeared in the IR spectrum of the studied sample in the region of 3.500 to 3.700 cm^{-1}, typical for stretching vibrations of associated OH-groups [8].

Thus, the mixing MgO with an aqueous solution of $MgCl_2$ leads to the formation of strong magnesium structures; this fact indicates its high chemical activity in the reactions of forming and hardening of magnesium cements.

The binding properties of the sludge were studied in the system sludge–H_2O, since $MgCl_2$ containing in the sludge interacting with water forms the internal solution

of magnesium chloride, and together with magnesium oxide it is involved into the formation of magnesia cement. The optimal mass ratio of water and sludge (S: L) is experimentally determined. The laboratory samples of magnesium cement formed from magnesium mixture with different ratio S: L, tested for strength characteristics (Fig. 3).

High values of the ultimate compressive strength were achieved in samples of 3- and 28-days of hardening time when the ratio of the magnesium mixture S: L = 0.37 (72.3 and 89.1 MPa, respectively). However, the setting time for such magnesium mixture was less than 5 min. Certainly, the mixture of sludge and water with such ratio cannot be used to prepare wood-mineral composition because of very short lifetime of the magnesium mixture.

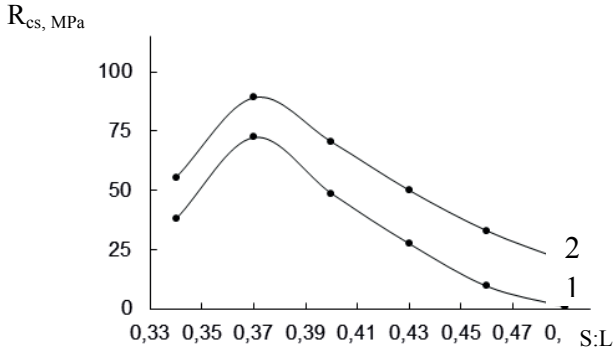

Fig. 3. Relation between ultimate compressive strength and (R_{cs}) and the ratio S: L for magnesium stone samples, formed in the system sludge — H_2O:
1 — 3-day hardening time and *2* — 28-day hardening time

The ratio of W: T = 0.43 is likely to be considered the optimal ratio when the start and finish of hardening time for the magnesium mixture is 20 and 40 min, respectively, this is typical for the formation of the magnesium mixture on the basis of caustic magnesite and magnesium chloride solution [14]. The ultimate compressive strength for samples of 3-and 28-day hardening time were 32.4 and 50.0 MPa.

The hardening process of magnesium cement being formed in the system at the optimum ratio of S: L has intensively run during the first 7 days (Fig. 1, curve 2). Similar shapes of the kinetic curves describing the hardening process of magnesium mixture in the open air indicates that adding water the sludge results to forming the $MgCl_2$ internal solution, which is involved into gaging MgO containing in the sludge with forming hydrate structures.

The formation of hydrated compounds containing in magnesium cement, obtained on the basis of the sludge and water at the optimum mass ratio, was confirmed by X-ray diffraction analysis. In the X-ray diffraction pattern of the 28-day hardening sample there is a number of both diffraction lines typical for the hydrate compounds $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ and $Mg(OH)_2$ and diffraction lines, d = 0.238, 0.192 and 0.183 nm, typical for the crystallohydrate $5Mg(OH)_2 \cdot MgCl_2 \cdot 2H_2O$. However, the concentration of magnesium pentoxihydrochloride is significantly lower in compared with trioxihydrochloride indicating involving magnesium oxide into the hydration as an intermediate metastable phase.

Mineral binders used in the construction material industry should comply with the radiation safety criteria in according to National State Standard (GOST) 30108–94 [15] and radiation safety standards NRB-99/2009 [16].

Specific effective radioactivity of the sludge is 430 $Bq \cdot kg^{-1}$ so the waste can be referred by radiation safety to the materials of class II. Composite mixture of the sludge and sawdust with weight ratio 1:1 shows 290 $Bq \cdot kg^{-1}$.Such construction mixes refer to the class I of danger on radiation safety so they are suitable for the manufacturing construction materials for residential and public buildings.

The toxicological tests of the sludge and its mixture with sawdust with weight ratio 1:1 showed that they are non-toxic. MgO and $KCl \cdot MgCl_2 \cdot 6H_2O$ are hygienic priorities in the sludge and its dust. The materials don't emit any chemical components to the air exceeding the threshold limit values (TLV). Sanitary-epidemiological conclusion certificate No.66.01.10.530 T. 000055.06.01 dated 02.07.2001 confirmed the compliance of the material to the state sanitary-epidemiological regulations.

The experimental results of the balance experiments to determine output of effective fractions when regenerating sludge, magnesium components and their mass ratio provided the basis for developing technology and the unit to recycle sludge to the magnesium binding powder.

Conclusion

The results of the comprehensive study of sludge forming in carnallite chlorinators while magnesium manufacturing allowed to conclude about the practical application of these wastes as technogenic raw materials to produce magnesium binders used instead of caustic magnesite in the technological processes of manufacturing wood mineral composites for construction applications.

References

1. Zyryanova V., Vereshchagin V., Isakova O., Logvinenko A. Synthesis chemically stable magnesium cement materials on the industrial waste basis. *Inorganic materials*, 1995, vol. 31, no. 1, pp. 1–4.

2. Fefelov N. K., Svit G. F. Using chloromagnesium salt alkali to produce a magnesia binder. *Environmental engineering. Recycling industrial waste into construction materials*. Sverdlovsk, 1984. P. 86.

3. Kudryavskiy Yu. P., Lipunov I. N., Panskiy. Processing of serpentinite raw materials — waste asbestos production to produce commercial products. *"Challenges and perspectives of*

developing the chemical technologies in the Western Urals". Perm, 2001, pp. 103–109.

4. Morachevskii Iu. V., Petrov E. M. *Metody analiza rassolov i solei* [Methods of analysis of brines and salts]. Moscow, Chemistry Publ., 1965. 368 p. (In Russ.).

5. *GOST 2642.8–97. Ogneupory i ogneupornoe syr'e. Metody opredeleniia oksida magniia* [State Standard 2642.8–97. Refractories and refractory raw materials. Methods for determination of magnesium oxide]. Moscow, Standartinform Publ., 2003. 8 p. (In Russ.).

6. Kovba L. M., Trunov V. K. *Rentgenofazovyi analiz* [X-ray diffraction]. Moscow, MSU Publ., 1976. 232 p. (In Russ.).

7. Wendlandt W. W. Thermal Methods of Analysis. John Wiley & Sons Inc., 1974. 524 p. (Russ. ed.: Uendlandt U. *Termicheskie metody analiza*. Moscow, Mir Publ., 1978. 526 p.).

8. Cross A. D. *An Introduction to Practical Infra-Red Spectroscopy*. London, 1960. (Russ. ed.: Kross A. *Vvedenie v prakticheskuiu infrakrasnuiu spektroskopiiu*. Moscow, Foreign Literature Publ., 1961. 110 p.).

9. Boldyrev V. V. *Methods to study the kinetics of thermal decomposition of solids*. Moscow, Metallurgizdat Publ., 1959. 132 p.

10. *GOST 310.3–76. Tsementy. Metody opredeleniia normal'noi gustoty, srokov skhvatyvaniia i ravnomernosti izmeneniia ob"ema* [State Standard 310.3–76. Cements. Methods for determination of standard consistency, times of setting and soundness]. Moscow, Standartinform Publ., 2003. 12 p. (In Russ.).

11. *GOST 8462–85. Materialy stenovye. Metody opredeleniia predelov prochnosti pri szhatii i izgibe* [State Standard 8462–85. Wall materials. Methods for determination of ultimate compressive and bending strength]. Moscow, Standartinform Publ., 2001. 8 p. (In Russ.).

12. Tarbeev Yu. V., ed. *Izmerenie aktivnosti radionuklidov* [Determination of radionuclide radioactivity]. Yekaterinburg, Poligrafist Publ., 1999. 397 p. (In Russ.).

13. Vyrodov I. P., Bergman A. G. K voprosu o tverdenii magnezial'nykh viazhushchikh [On hardening of chloromagnesium cements]. *Zhurnal prikladnoi khimii — Journal of Applied Chemistry*, 1959, vol. 32, issue 3, pp. 504–509. (In Russ.).

14. Kolbasov V. M., Leonov I. I., Sulimenko L. M. Tekhnologiia viazhushchikh materialov [Technology of binding materials]. Moscow, Stroyizdat Publ., 1987. 432 p. (In Russ.).

15. *GOST 30108–94. Materialy i izdeliia stroitel'nye. Opredelenie udel'noi effektivnoi aktivnosti estestvennykh radionuklidov* [State Standard 30108–94. Building materials and elements. Determination of specific activity of natural radioactive nuclei]. Moscow, Standartinform Publ., 2007. 8 p. (In Russ.).

16. *NRB-99. Normy radiatsionnoi bezopasnosti* [Radiation Safety Standards]. Moscow, Minzdrav RF, 1999. 116 p.